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First observation of capping/uncapping by a ligand of a Zn porphyrin adsorbed on Ag(100)

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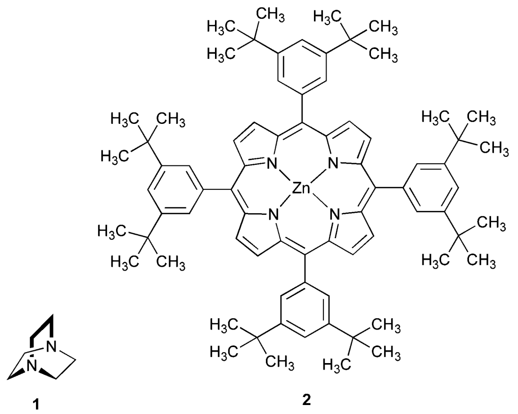
A significant first step towards creation of catalytically active porphyrin-functionalised metal surfaces has been achieved.

The structure and properties of metalloporphyrins adsorbed at solid surfaces are of great topical interest due to the distinctive chemical and electronic properties of these versatile molecules. Self-assembled layers have been investigated as potential light-harvesting arrays, optical switches and photonic wires.[1] Supramolecular arrays are of interest with respect to the study of energy transfer and photosynthetic mechanisms;[2] two-dimensional assemblies have attracted much attention for application as sensors or other types of molecular devices.[3] Here we are concerned with a different aspect of this field—the possibility of harnessing the intrinsic chemistry of a tethered metalloporphyrin to the complementary chemistry of the surface upon which it is adsorbed. The goal is to devise heterogeneous systems that are effective in the catalysis of delicate organic reactions (*e.g.* alkane hydroxylation, alkene epoxidation) that currently can only be carried out by means of homogeneous catalysis. The present communication describes a first step in this direction, namely the creation of a porphyrin-functionalised catalytically significant (silver) surface that exhibits ligand binding/unbinding reactions characteristic of the free metalloporphyrin.

In solution, zinc porphyrins and the bidentate ligand DABCO are capable of reversibly forming a variety of supramolecular complexes.[4] Here, by means of STM, we show that this homogeneous chemistry can be mimicked by Zn-TBPP (Scheme 1) adsorbed at the Ag(100) surface. The structure of the porphyrin was deliberately chosen so as to minimise interaction between the macrocycle and the metal surface precisely with the object of *avoiding* the formation of dense highly ordered structures. Such dense layers would block the co-adsorption of reactants on the metal surface and hence would be catalytically inert towards the kinds of processes that are our goal—metal-mediated porphyrin-catalysed reactions. In other words, the structures we aim for are of just the opposite kind to those that are usually investigated.

Experiments were carried out in an Omicron UHV STM. Zn-TBPP was deposited by evaporation under UHV (source temperature 573 K) onto the clean atomically flat Ag(100) surface held at 298 K. This resulted in nucleation and growth of 3D aggregates of Zn-TBPP molecules with dimensions of the order of 20 nm × 20 nm. Subsequent annealing to 523 K for 60 min served to distribute the Zn-TBPP molecules across the surface. A typical result is illustrated in Fig. 1 which shows the STM image acquired at 298 K. No significant changes in image contrast as a function of tip bias or polarity were observed.



Scheme 1 Structures of 1,4-diazabicyclo[2.2.2]octane (DABCO) **1** and of Zn tetra-[3,5-di-*t*-butylphenyl]porphyrin (Zn-TBPP) **2**.

The individual Zn-TBPP molecules are observed as symmetric four-lobed entities, each lobe corresponding to one of the four di-*t*-butylphenyl groups.[5] The molecules exhibit an apparent height of ~0.8 Å and an apparent diameter of ~20 Å, in agreement with observations on related systems. The adsorption geometry corresponds to the porphyrin ring being oriented parallel to the Ag surface (see top curve in Fig. 2(D) which is a line scan through a single molecule). Note that the molecules are distributed randomly on the terraces with no strongly preferred orientation with respect to the underlying metal lattice, despite the fourfold rotational symmetry of both adsorbate and substrate. Neither is there any apparent long range order. The same general behaviour was found over the entire range of coverage. This behaviour, which is exactly what is desired, is consistent with the di-*t*-butylphenyl groups at the *meso* positions lying essentially orthogonal to the plane of the macrocycle, thus inhibiting strong electronic interaction between the molecular π electron system and the Ag surface.

Figs. 2(A)–(C) show a sequence of images of Zn-TBPP covered Ag(100) taken after exposure at 123 K to increasing amounts of DABCO. Fig. 2(A) shows the result of dosing the porphyrin covered surface with 50 L (1 L = 1.33×10^{-6} mbar s) of DABCO, (B) was acquired after a further exposure of 140 L and (C) shows the result of warming system (B) to 298 K. (Control experiments showed that DABCO does not adsorb on clean Ag(100) at 123 K.) The sequence (A)–(B)–(C) could be repeated many times on the same porphyrin covered surface. It is clear that treating the adsorbed porphyrin with DABCO results in a reaction that is reversible with temperature. The circles indicate three distinct types of features with similar lateral dimensions, but exhibiting different *z*-contrast. Typical height profiles of these features are shown in Fig. 2(D). All three entities are characterised by apparent diameters

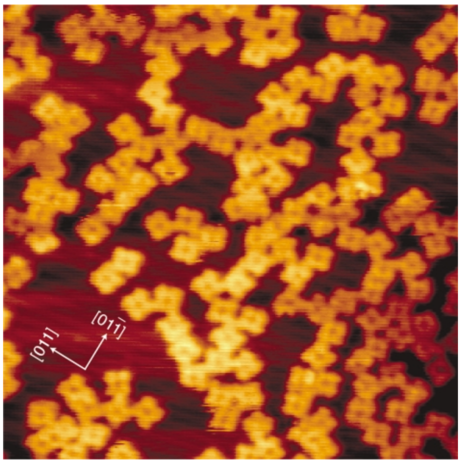


Fig. 1 STM image of Zn-TBPP molecules adsorbed on Ag(100) at 298 K, $V = 0.75$ V, $I = 0.1$ nA, 200 Å × 200 Å.

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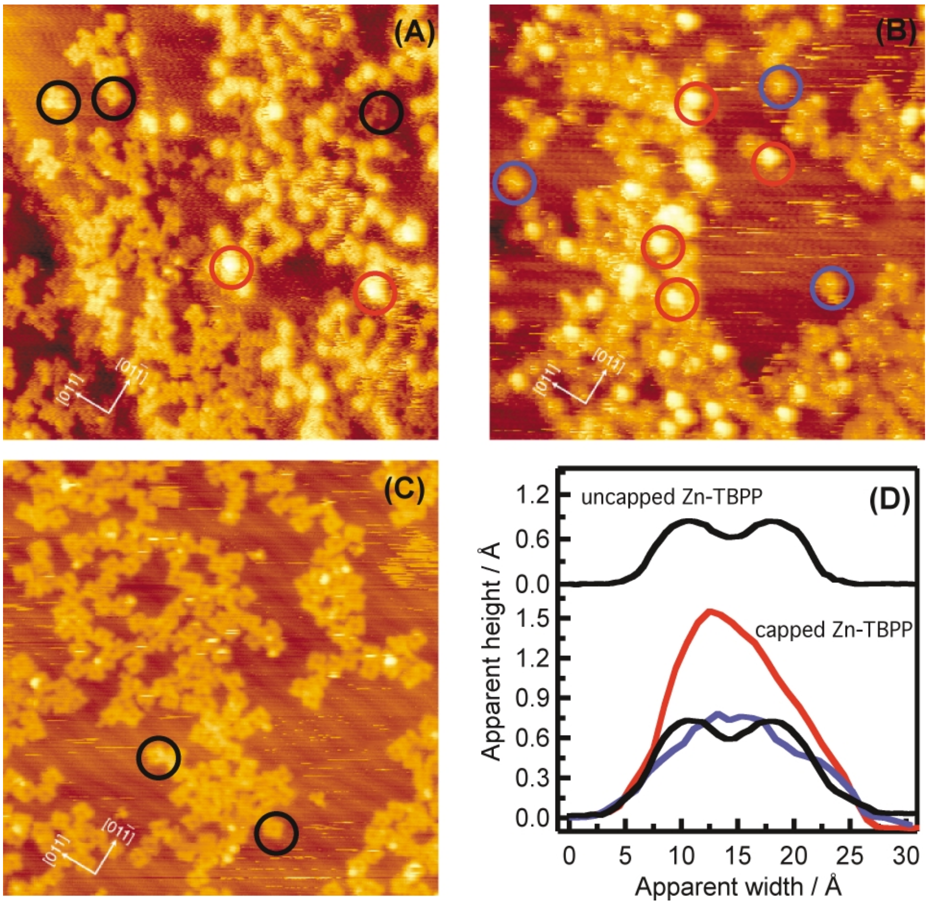

Fig. 2 Sequence of STM images of Zn-TBPP on Ag(100) taken at 123 K after: (A) dosing 50 L of DABCO, (B) dosing 140 L of DABCO and (C) after (B) at room temperature (V = 1.5 V, I = 0.1 nA, 300 Å × 300 Å). Typical height profiles of the features marked with circles are shown in (D).

of ~20 Å. The features circled in black and blue have apparent heights of ~0.8 Å whereas those circled red have an apparent height of 1.5 Å. Notice that the number density of the "red" features increases with increasing exposure to DABCO—suggesting that they are due to a Zn-TBPP–DABCO complex. The black circles correspond to bare Zn-TBPP molecules exhibiting the characteristic four distinct lobes. This assignment is confirmed by the corresponding (black) line scan shown in the lower part of Fig. 2(D) which is to be compared with that obtained from a Zn-TBPP molecule on the DABCO-free surface (top curve in Fig. 2(D)). The "red" entities exhibit the greatest height. Their appearance is consistent with porphyrin molecules capped by DABCO molecules axially located over the Zn atom with which they interact *via* the nitrogen lone pair. This chemical behaviour and its reversibility closely parallels that of free Zn-TBPP interacting with DABCO in solution,[4] pointing to the feasibility of devising metal surface tethered porphyrins in which the intrinsic chemistry of the porphyrin is preserved. The general appearance of the "blue" features in Fig. 2(D) (lower panel) is similar to that of the Zn-TBPP–DABCO complex, but their height is less. They are assigned to Zn-TBPP–DABCO complexes that have undergone electron-induced decomposition under the influence of the STM tip.[6]

In summary, binding/unbinding of DABCO by Zn-TBPP adsorbed on the Ag(100) surface has been demonstrated. The results represent a significant first step on the way to the creation of porphyrin-functionalised surfaces capable of carrying out delicate and selective heterogeneously catalysed reactions of the type normally associated with homogeneous systems.

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